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(21) International Application Number: PCT/EP98/00391 (22) International Filing Date: 21 January 1998 (21.01.98) (30) Priority Data: 97200283.6 3 February 1997 (03.02.97) EP <i>(34) Countries for which the regional or international application was filed:</i> NL et al. (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): SCHUURMAN, Pieter [NL/NL]; Molecaten 45, NL-3772 LH Barneveld (NL). VAN SWIETEN, Andreas, Petrus [NL/NL]; Reinaldstraat 6, NL-6883 HM Velp (NL). HOGT, Andreas, Herman [NL/NL]; Deurningerstraat 58, NL-7514 BJ Enschede (NL). DE VRIES, Bernhard [NL/NL]; Harderwijkerweg 106, NL-8071 GD Nunspeet (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PEROXIDE COMPOSITIONS WITH IMPROVED SAFETY CHARACTERISTICS (57) Abstract <p>Safe peroxide compositions are provided which comprise two phlegmatizers having boiling points that are more than 20 °C, preferably more than 50 °C, apart. These compositions are safer than peroxide compositions with the same peroxide concentration containing only one phlegmatizer or phlegmatizers not fulfilling the boiling point requirement. The compositions are particularly useful in radical polymerization processes, cross-linking reactions, polymer modification processes, and other reactions involving peroxides, for example the preparation of certain chemicals.</p>		

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PEROXIDE COMPOSITIONS WITH IMPROVED SAFETY CHARACTERISTICS

5 FIELD OF THE INVENTION

The present invention relates to liquid formulations of peroxides that need to be phlegmatized in order to fulfill safety requirements.

10 BACKGROUND OF THE INVENTION

Numerous peroxides are known that need to be phlegmatized with an inert diluent or solvent in order to permit their safe handling and use. For some peroxides, to meet all safety regulations and to allow storage, shipment,
15 and handling in an acceptable, safe fashion, the concentration of active oxygen in the final formulation must be very low. However, such formulations with low peroxide concentrations are mostly undesirable, since the application of the formulation will lead to high levels of undesired inert diluent or solvent in the resulting material.

20.

U.K. Patent 1,072,728 discloses specific ketone peroxides formulations comprising at least one particular hydrophilic solvent that renders the formulation safe. It is not suggested that other combinations of solvents, not being the hydrophilic solvents in suit, would permit safe peroxide
25 compositions with an even higher active oxygen content.

U.S. Patent 3,649,546 relates to non-hazardous ketone peroxide polymerization initiators wherein ketone peroxides are formulated in esters with boiling points in the range of 140-250°C. Such compositions may also

contain another compatible diluent. No reference is made to any requirements in respect of the boiling point of the additional diluent, nor to any advantages that specific combinations of phlegmatizer and diluent may have.

5

The ketone peroxide formulations as described in both U.K. Patent 1,072,728 and U.S. Patent 3,649,546 suffer from the fact that the esters and hydrophilic phlegmatizers that are used therein, have a negative effect on the unsaturated polyester resins wherein they are typically applied for curing. More particularly, in gel coats, the disclosed ketone peroxide formulations will often lead to an increased osmosis and to the related blistering problems, because of the compatibility of the phlegmatizer and water.

15 U.K. Patent 1,470,012 discloses specific ketone formulations that are considered to be safe and whereof the specified solvent system must boil smoothly over a range of at least 40°C at temperatures of at least 175°C. Also in this reference, the solvents of choice are glycols and phosphates, that can be classified as hydrophilic materials.

20

U.S. Patent 4,052,464 discloses the preparation of di-tert.butylperoxy ketals using ethylbenzene as a reaction medium to enable the azeotropic removal of water. Additionally, the reaction medium may contain a diluent having a boiling point higher than that of ethylbenzene. However, no benefits of such a combination are given.

25

U.S. Patents 4,131,728 and 4,178,263 disclose how shock sensitive peroxides may be phlegmatized using at least one non-homopolymerizing (co)monomer as a diluent, whereas in International patent application WO 93/25615 the use of oligomers of styrene and a comonomer as a diluent for

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such peroxides is described. Advantages associated with particular combinations of diluents are not disclosed or suggested.

From the above it is clear that the formulation of peroxides has long been receiving considerable attention. The main goal has been to formulate compositions that allow safe manufacture, transportation, storage, and handling. Additionally, it has been attempted to formulate peroxide compositions with as high an active oxygen content as possible, preferably based on diluents that do not adversely affect the material produced with the peroxide composition.

SUMMARY OF THE INVENTION

It has unexpectedly been found that a combination of phlegmatizers with boiling points that are at least 20°C, preferably more than 50°C, apart, permits the formulation of safer peroxide compositions. One of the phlegmatizers may be a solid or wax, provided that the final composition including peroxide, the phlegmatizers and optional other additives is in liquid form at handling temperatures. Preferably, the liquid composition is homogeneous, although one of the phlegmatizers may also be in a finely dispersed form, for example in suspension, emulsion, or vesicle form.

Accordingly, the present invention provides in a first aspect, safer peroxide compositions comprising at least two phlegmatizers that have boiling points more than 20°C, preferably more than 50°C, apart, with an active oxygen concentration greater than the active oxygen concentration of compositions with acceptable characteristics based on one phlegmatizer or two phlegmatizers not satisfying the boiling point requirement.

In a second aspect, the present invention relates to the use of these compositions in radical polymerization processes, including curing reactions of unsaturated polyester resins, cross-linking reactions, polymer modification processes, and other reactions involving peroxides, like the
5 synthesis of certain chemicals. By applying the peroxide compositions according to the invention, less phlegmatizer is introduced into the various applications, either allowing higher peroxide loads in the process or generating products with improved properties.

10 In a third aspect, the present invention relates to, preferably non-cyclic, ketone peroxide compositions that comprise no hydrophilic phlegmatizers or reduced levels thereof, but mainly so-called apolar phlegmatizers. Such formulations allow the production of unsaturated polyester resin articles with increased resistance to osmosis.

15 In yet another aspect, the present invention relates to safe, preferably non-cyclic, ketone peroxides having a reduced viscosity for use in spray-on processes of unsaturated polyester resins. This and other objects of the invention will be apparent from the summary and detailed description which
20 follow.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention are safer than compositions of
25 the same peroxide with the same peroxide concentration in which use is made of only one phlegmatizer or of two phlegmatizers not satisfying the boiling point requirement as specified herein. By "safer" is meant that the compositions of the present invention show an improvement in at least one

of the following tests:

- deflagration test (deflagration),
- the time pressure test (deflagration),
- the Koenen test (heating under defined confinement), and
- 5 - the pressure vessel test (heating under defined confinement).

Improvement means a lower rating in the test result; or , alternatively, for the deflagration test a change from "yes, rapidly" to "yes, slowly" or from "yes, slowly" to "no"; for heating under defined confinement a change from "violent" to "medium", from "medium" to "low", or from "low" to "no".

10

The safety tests and corresponding criteria are documented as UN test C.1 for the time pressure test, UN test C.2 for the deflagration test, UN test E.1 for the Koenen test and UN test E.2 for the pressure vessel test in the "United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.2", United Nations, 15 New York and Geneva, 1995.

The peroxide compositions according to the invention are characterized by the use of at least two phlegmatizers, with the conditions that 1) for at least one out of all possible pairs of phlegmatizers the difference in boiling point 20 is more than 20°C, preferably more than 50°C and 2) the final composition shows no or slow deflagration in the deflagration test and the time pressure test and no violent thermal explosion effects are observed in the pressure vessel test and/or the Koenen test.

25

The phlegmatizer with the lowest boiling point should have a boiling point such that no or slow deflagration of the peroxide composition occurs in the deflagration and time pressure test. Preferably the boiling point lies between 30°C and 300°C, more preferably between 100°C and 250°C. 30 Most preferred are boiling points between 100°C and 200°C. Acceptable

boiling points for the low-boiling phlegmatizer will depend on the peroxide to be formulated, the concentration of the peroxide in the composition, and the concentration of the low-boiling phlegmatizer. Whenever rapid deflagration occurs in the deflagration or the time pressure test, the concentration of the peroxide has to be decreased, the concentration of the low-boiling phlegmatizer has to be increased, or a phlegmatizer with a lower boiling point has to be used. Similarly, whenever the composition passes both the deflagration test and the time pressure test, the peroxide concentration in the composition may be increased, the concentration of the low-boiling phlegmatizer may be decreased, or a phlegmatizer with a higher boiling point may be used.

When non-cyclic ketone peroxides are phlegmatized, preferably the low-boiling phlegmatizer is to be limited to apolar materials. Apolar phlegmatizers are all solvents that have little affinity for water. In this document apolar phlegmatizers are defined to be solvents that are not alcohols, including glycols, esters, and/or cyclic amides.

The phlegmatizer with the highest boiling point is selected such that the composition passes both the pressure vessel test (PVT) and the Koenen test, i.e., no violent thermal explosion effect is observed in any of these tests under any of the circumstances. This high-boiling phlegmatizer should have a boiling point at least 20°C, preferably 50°C, above that of the phlegmatizer with the lowest boiling point. Preferably, the boiling point of the high-boiling phlegmatizer lies between 100°C and 700°C, more preferably between 200°C and 600°C. Acceptable boiling points for the high-boiling phlegmatizer will depend on the peroxide to be formulated, the concentration of the peroxide, and the concentration of the high-boiling phlegmatizer. Whenever the composition does not pass the PVT or the Koenen test, the peroxide concentration has to be decreased, the concentration of high-boiling phlegmatizer has to be increased, or a

phlegmatizer with a higher boiling point has to be selected. Similarly, whenever the composition passes both the PVT and Koenen tests, the peroxide concentration may be increased, or the high-boiling phlegmatizer concentration decreased or a phlegmatizer with a lower boiling point may
5 be selected in order to obtain the desired composition.

With this information, the skilled person will have no problem in formulating peroxide compositions with a peroxide concentration higher than would have been acceptable if only one phlegmatizer, or two or more
10 phlegmatizers not satisfying the boiling point requirement, were used. Any weight ratio between low- and high-boiling phlegmatizer in the composition can be applied. Preferred are weight ratios of low- and high-boiling phlegmatizers between 20:1 and 1:20. More preferred are weight ratios between 10:1 and 1:10. Most preferred are weight ratios between 5:1 and
15 1:5.

Whenever a phlegmatizer does not exhibit one specific boiling point, the median of the boiling range is to be substituted for it.

20 In a further embodiment of the invention, existing combinations of peroxides with one phlegmatizer can be improved by applying a second phlegmatizer that has a boiling point that differs more than 20°C, preferably more than 50°C, from the boiling point of the first phlegmatizer. In such new compositions higher peroxide concentrations can be used while safety
25 characteristics are not regressed.

Peroxides that can be formulated according to the invention include peroxyesters, percarbonates, peroxydicarbonates, diacylperoxides, peroxyketals, hydroperoxides, and ketone peroxides. These peroxides are
30 either liquid at room temperature or dissolved in the phlegmatizers

according to the invention. Examples of specific peroxides that are illustrative of these classes of peroxides are tertiary alkyl peracetates, peroxyketals derived from linear, branched or cyclic C₃-C₁₃ ketones or C₄-C₂₀ diketones, and ketone peroxides derived from linear, branched or cyclic C₃-C₁₃ ketones or C₄-C₂₀ diketones. The hydroperoxide that is used in the preparation of the peroxide may not only be aliphatic, but may, optionally, be unsaturated and may also comprise one or more cycloaliphatic or aromatic groups. Also, the hydroperoxide may contain one or more hydroperoxy groups.

10

More preferably, the invention pertains to compositions of ketone peroxides that contain at least two phlegmatizers. The ketone peroxides may be either cyclic or non-cyclic. Preferably, at least the lowest boiling phlegmatizer therein is apolar. The ketone peroxides can be made by reacting a ketone with hydrogen peroxide as is described in U.S. Patent 3,003,000; Uhlmann, 3rd Edition, Vol. 13, pp. 256-57 (1962); the article, "Studies in Organic Peroxides. XXV. Preparation, Separation and Identification of Peroxides Derived from Methyl Ethyl Ketone and Hydrogen Peroxide," Milas, N.A. and Golubovic, A., J. Am. Chem. Soc., Vol. 81, pp. 5824-26 (1959), Organic Peroxides, Swern, D. editor, Wiley-Interscience, New York (1970), and Houben-Weyl Methoden der Organische Chemie, E13, Volume 1, page 736, the disclosures of which are hereby incorporated by reference.

25

Suitable ketones for use in the synthesis of ketone peroxides include, for example, acetone, acetophenone, methyl-n-amyl ketone, ethylbutyl ketone, ethylpropyl ketone, methylisoamyl ketone, methylheptyl ketone, methylhexyl ketone, ethylamyl ketone, diethylketone, dipropyl ketone, methylethyl ketone, methylisobutyl ketone, methylisopropyl ketone, methylpropyl ketone, methyl-n-butyl ketone, methyl-t-butyl ketone,

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isobutylheptyl ketone, diisobutyl ketone, cyclohexanone, 2-methyl cyclohexanone, 3,3,5-trimethyl cyclohexanone, methylbenzyl ketone, phenylmethyl ketone, phenylethyl ketone, methylchloromethyl ketone, methylbromomethyl ketone, 1-phenyl-pentanedione-2,4, cyclohexanedione-1,4, and coupling products thereof. Also mixtures of two or more different ketones can be used.

Examples of suitable peroxides for use in accordance with the present invention are the (cyclic) ketone peroxides derived from acetone, acetylacetone, methylethyl ketone, methylpropyl ketone, methylisopropyl ketone, methylbutyl ketone, methylisobutyl ketone, methylamyl ketone, methylisoamyl ketone, methylhexyl ketone, methylheptyl ketone, diethyl ketone, ethylpropyl ketone, ethylamyl ketone, methyloctyl ketone, methylnonyl ketone, methyldecyl ketone, methylundecyl ketone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, 3,3,5-trimethyl cyclohexanone, and mixtures thereof. Cyclic ketone peroxides are composed of at least two ketone peroxide entities which may be the same or different. Thus, cyclic ketone peroxides may be in the form of dimers, trimers, etc. When cyclic ketone peroxides are prepared, usually a mixture is formed which predominantly consists of the dimeric and trimeric forms. The ratio between the various forms mainly depends on the reaction conditions during the preparation. If so desired, the mixture may be separated into the individual cyclic ketone peroxide compounds. Generally, the cyclic ketone peroxide trimers are less volatile and more reactive than the corresponding dimers. Preference for certain compositions or individual compounds may depend on differences in physical properties or requirements in application of the peroxides, e.g. storage stability, half-life time versus temperature, volatility, boiling point, solubility, etc.. It is to be understood that any form of the cyclic ketone peroxides, e.g. oligomeric compounds or mixtures, is comprised in the present invention. Preferably,

the cyclic ketone peroxide is produced using an apolar solvent like a hydrocarbon. Most preferred phlegmatizers used in the production of the cyclic ketone peroxide are selected from white oils and isoaliphatic hydrocarbons.

5

Examples of useful liquid phlegmatizers that can be used in the compositions according to the invention include various solvents, diluents and oils. More particularly, useful liquids include alkanols, cycloalkanols, alkylene glycols, alkylene glycol monoalkyl ethers, cyclic ether substituted

10 alcohols, cyclic amides, aldehydes, ketones, epoxides, esters, hydrocarbon solvents, halogenated hydrocarbon solvents, paraffinic oils, white oils, and silicone oils.

Examples of hydrophilic esters include, but are not limited to,

15 monocarboxylic esters of mono- and dihydric alcohols, esters of dicarboxylic acids and monohydric alcohols, carbonates of monohydric alcohols, alkoxyalkyl esters, β -keto esters, phthalates, phosphates, benzoates, adipates, and citrates.

20 More specific examples of esters useful in most of the compositions of the present invention are dimethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, dibenzyl phthalate, butyl benzyl phthalate, diallyl phthalate, n-pentyl acetate, isopentyl acetate, n-hexyl acetate, 2-ethylhexyl acetate, benzyl acetate, methyl benzoate, ethyl benzoate,

25 isopropyl benzoate, n-octyl benzoate, isodecyl benzoate, diethylene glycol dibenzoate, dipropylene glycol dibenzoate, propylene glycol dibenzoate, n-butyl pivalate, isoamyl pivalate, sec-amyl pivalate, n-hexyl pivalate, diethyl adipate, dioctyl adipate, diisodecyl adipate, methyl neodecanoate, n-butyl neodecanoate, propylene glycol diacetate, ethylene glycol diacetate,

30 cyclohexyl acetate, neopentyl acetate, methyl-2-ethylhexanoate, n-heptyl

formate, n-octyl formate, dipropyl carbonate, dibutyl carbonate, isoamyl propionate, sec-amyl propionate, benzyl propionate, butyl caproate, ethylene glycol dipropionate, heptyl propionate, methylphenyl acetate, octyl acetate, 2-ethylhexyl acetate, propyl caprylate, triethyl phosphate, tricresyl phosphate, trixylyl phosphate, cresyl diphenyl phosphate, 2-ethylhexyl-diphenyl phosphate, isodecyl-diphenyl phosphate, tri(2-ethylhexyl) phosphate, dimethyl methylphosphonate, chlorinated phosphate esters, tributyl phosphate, tributoxyethyl phosphate, methyl decanoate, dimethyl succinate, diethyl succinate, dimethyl malonate, diethyl malonate, methylethyl succinate, diisobutyl nylonate, 2,2,4-trimethyl-1,3-pentanediol-diisobutyrate, diethyl oxalate, methyl p-toluate, dimethylfumarate, diethylfumarate, dipropylfumarate, dibutylfumarate, acetyltributyl citrate and diesters of maleicanhydride, like dibutylmaleate.

Preferred useful hydrocarbon solvents include, but are not limited to, hydrogenated oligomers of alkanes, pentane, heptane, isododecane, toluene, ethylbenzene, xylene (o, m, p, or mixtures thereof), mesitylene, amyl benzene, isoamyl benzene, decalin, o-diisopropyl benzene, m-diisopropyl benzene, p-diisopropyl benzene, n-dodecane, 2,4,5,7-tetramethyl octane, n-amyl toluene, 1,2,3,4-tetramethyl benzene, 3,5-diethyl toluene, hexahydronaphthalene, and mixtures thereof. More preferred hydrocarbon solvents include Isopar® B, Isopar C, Isopar E, Isopar H, Isopar J, Isopar K, Isopar L, Isopar M, Isopar V, Exxsol® hexane, Exxsol heptane, Exxsol D145/160, Exxsol D40, Varsol® 40, Varsol 60, Solvesso® 100, Solvesso 150, Solvesso 200, Shellsol® T, Shellsol TD, Shellsol D40, Shellsol D60, Shellsol D70, Shellsol D90, Shellsol D100 and mixtures thereof.

Useful halogenated hydrocarbons include phenyl trichloride, 3-bromo-o-xylene, 4-bromo-o-xylene, 2-bromo-m-xylene, 4-bromo-m-xylene, 5-bromo-

m-xylene, o-dibromobenzene, p-dibromobenzene, 1,4-dibromobutane, 1,1-dibromo-2,2-dichloroethane, bromooctane, tetrabromoethylene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and mixtures thereof.

- 5 Examples of aldehydes useful in the compositions of the present invention include n-chlorobenzaldehyde and decanal.

- Examples of ketones useful in the compositions of the present invention include acetophenone, isophorone, isobutyl ketone, methylphenyl diketone,
10 diamyl ketone, diisoamyl ketone, ethyloctyl ketone, ethylphenyl ketone, acetone, methyl-n-amyl ketone, ethylbutyl ketone, ethylpropyl ketone, methylisoamyl ketone, methylheptyl ketone, methylhexyl ketone, ethylamyl ketone, diethyl ketone, dipropyl ketone, methylethyl ketone, methylisobutyl ketone, methylisopropyl ketone, methylpropyl ketone, methyl-t-butyl ketone,
15 isobutylheptyl ketone, diisobutyl ketone, 2,4-pentanedione, 2,4-hexanedione, 2,4-heptanedione, 3,5-heptanedione, 3,5-octanedione, 5-methyl-2,4-hexanedione, 2,6-dimethyl-3,5-heptanedione, 2,4-octanedione, 5,5-dimethyl-2,4-hexanedione, 6-methyl-2,4-heptanedione, 1-phenyl-1,3-butanedione, 1-phenyl-1,3-pentanedione, 1,3-diphenyl-1,3-propanedione,
20 1-phenyl-2,4-pentanedione, cyclohexanedione-1,4, methylbenzyl ketone, phenylethyl ketone, methylchloromethyl ketone, methylbromomethyl ketone and coupling products thereof.

- Examples of cyclic amides include 2-pyrrolidone, N-methyl pyrrolidone, 1,5-
25 dimethyl-2-pyrrolidone, and 3,3-dimethyl-2-pyrrolidone.

An example of an epoxide which may be employed in the compositions of the present invention is styrene oxide.

Examples of useful alcohols are n-butyl alcohol, capryl alcohol, octyl alcohol, dodecyl alcohol, tetrahydrofurfuryl alcohol, 1,4-dihydroxymethyl cyclohexane, cyclohexanol, glycerol, ethylene glycol, diethylene glycol, polyethylene glycols with molecular weights under 20,000, propylene glycol, dipropylene glycol, neopentyl glycol, hexylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, butene diol, 1,5-pentane diol, 3,6-dimethyloctane-3,6-diol, 2,5-dimethyl-hex-3-yne-2,5-diol, 2,4,7,9-tetramethyldecane-4,7-diol, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether.

The paraffinic oils useful in the compositions of the present invention include, but are not limited to, halogenated paraffinic oils and paraffinic diesel oil.

Other oils, including white oils, epoxidized soybean oils, and silicone oils, are also useful in the compositions of the present invention. Preferred white oils include, but are not limited to, Marcol® 52, Marcol 82, Marcol 172, Primol® 352, and Bayol® 82.

Soluble solid or waxy materials that can be employed in the compositions of the present invention include solid paraffins, polyethylene glycol, polypropylene glycol, polytetrahydrofuran, and polycaprolactone.

The compositions of the present invention may also contain optional other additives as long as these additives do not have a significant negative effect on the safety, transportability and/or storage stability of the formulations. As examples of such additives may be mentioned: antiozonants, antioxidants, antidegradants, U.V. stabilizers, coagents, fungicides, antistatic agents, pigments, dyes, coupling agents, dispersing

aids, blowing agents, lubricants, process oils and mould-release agents. These additives may be employed in their usual amounts.

More preferred compositions in accordance with the present invention
5 contain 10-90% by weight of one or more of the (cyclic) ketone peroxides, and most preferably these compositions contain 20-70% by weight of the (cyclic) ketone peroxides.

The compositions of the present invention are useful in conventional radical
10 (co)polymerization processes as well as for curing unsaturated polyester resins and for cross-linking, degradation or other types of modification processes of (co)polymers. An important advantage is obtained by using the compositions according to the invention because they are safer and/or they show a higher peroxide content. When using compositions with a
15 higher peroxide content, there will be less contamination of the polymer with the phlegmatizing agents that are used. Hence polymers of improved quality are attainable.

When the compositions according to the invention are used in processes
20 involving the curing of unsaturated polyester resins, the peroxides are preferably selected from cyclic or non-cyclic ketone peroxides, while the phlegmatizers are preferably selected from apolar products such as aldehydes, ketones, epoxides, (halogenated) hydrocarbon solvents, paraffinic oils, white oils, silicone oils, and combinations thereof. Most
25 preferably, the phlegmatizers are selected from (halogenated) hydrocarbon solvents, paraffinic oils, white oils, and combinations thereof. The use of such apolar compounds in the composition is observed to improve the resistance of the cured resin to osmosis. Osmosis is the process where water penetrates the surface of the cured resin product, often a gel coat,
30 and forms sub-surface pockets that are visible on the surface as "blisters".

Osmosis is known to be a very serious problem for polyester resin based boat hulls.

To prevent osmosis, alternatively the apolar phlegmatizer is combined with one phlegmatizer that is more hydrophilic in nature, so that at least one of the phlegmatizers is apolar. Preferably, this apolar phlegmatizer is the low-boiling one. Depending on the type of peroxide and the types of phlegmatizers used, as well as the concentration of these compounds in the composition, the compositions, when used in the curing process of unsaturated polyester resins, will result in cured resins that hardly suffer from osmosis.

Furthermore, it was observed that many of the safe compositions according to the invention have a reduced viscosity compared with commercial ketone peroxide formulations comprising a conventional hydrophilic phlegmatizer. Such a reduced viscosity is highly desired in processes where an unsaturated polyester resin is used in spray-on techniques. Preferably, at least one of the phlegmatizers of the composition is apolar, since such compositions showed substantially reduced viscosities and very good blending into unsaturated polyester resin.

20

The present invention will be further illustrated by the following examples, which are not to be construed as limiting the invention in any way.

EXAMPLESMaterials employed

Peroxides:

- 5 - Cyclic Methyl ethyl Ketone Peroxide (cyclic-MEKP) with a total active Oxygen concentration of 10.63%.
- 2,2-Di(tert-butylperoxy)butane (DTBPB), 80%
- tert-Butylperoxy acetate (TBPA), 70%
- Methyl Ethyl Ketone Peroxide with DMP (MEKP), act.O 11.63%

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Phlegmatizers :	Boiling point (°C)	Flashpoint (°C):
- Isopar E	125	7
- Xylene	140	28
- Isododecane	185	45
15 - Diethylene glycol	245	
- Isopar V	292	132
- Dimethylphthalate (DMP)	284	200
- Primol®352 white oil (ex. Exxon)	477	250

20 Miscellaneous

Total active oxygen contents of peroxide compositions can be determined with conventional techniques. For cyclic active oxygen (act. O) content analysis in ketone peroxides reference is made to procedures as described

25 in European Patent Application 94202136.1.

The determination of the dimer/trimer ratio (D/T) in cyclic-ketone peroxides can be accomplished by GC techniques as described in European Patent Application 94202136.1.

30

Procedures and criteria in respect of the time pressure test, the deflagration test, the Koenen test, and the pressure vessel test are disclosed in UN test C.1, UN test C.2, UN test E.1, and UN test E.2, respectively, in "United Nations Recommendations on the Transport of Dangerous Goods, Manual
5 of Tests and Criteria, ST/SG/AC.10/11/Rev.2", United Nations, New York and Geneva, 1995.

Examples 1-3 and Comparative Examples A and B

	Ex. 1	Ex. 2	Ex. 3	Ex. A	Ex. B
Cyclic MEK content (act. O)	6 %	6 %	6 %	6 %	6 %
D/T	9.5/90.5	10/90	6/94	17/82	25/75
Phlegmatizer, weight ratio *	A:B=1:1	A:B=3:1	A:B=9:1	A	B
PVT, rating	2 mm, low	2 mm, low	4 mm, medium	8 mm, medium	14 mm, violent
Koenen test rating	< 1 mm, low	< 1 mm, low	< 1 mm, low	< 1 mm, low	< 1 mm, low
Deflagration test, rating	0.21 mm/s, no	0.24 mm/s, no	4,34 mm/s, yes slowly	3,9 mm/s, yes slowly	0.02 mm/s, no
TPT, rating	< 20.7 bar, no	<20.7 bar, no	770 ms, yes slowly	<20.7 bar, no	<20.7 bar, no

* Phlegmatizer A is Primol®352

Phlegmatizer B is Isododecane.

5

The formulation according to the invention has acceptable safety properties, whereas the single solvent based recipes have not.

Example 4 and Comparative Examples C and D

	Example 4	Example C	Example D
DTBPB content	60%	60%	60%
Phlegmatizer, weight ratio *	C:D = 1:1	C	D
PVT, rating	6 mm, medium	6 mm, medium	22 mm, violent
Koenen test, Rating	1.5 mm, medium	1.5 mm, medium	10 mm, violent
Deflagration test, rating	0.289 mm/s, no	0.694 mm/s, yes slowly	0 mm/s, no
TPT, rating	1997 ms, yes slowly	2227 ms, yes slowly	< 20.7 bar, no

* Phlegmatizer C is Isopar V.

Phlegmatizer D is Isopar E.

5

The PVT rating of the peroxide formulation with Isopar E is not acceptable. The composition according to the invention has an improved performance in the deflagration test when compared with the formulation with only Isopar V.

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Example 5 and Comparative Examples E and F

	Example 5	Example E	Example F
TBPA content	60%	60%	60%
Phlegmatizer, weight ratio *	E:F = 1:3	E	F
PVT, rating	6 mm, medium	> 24 mm, violent	7 mm, medium
Koenen test, rating	1 mm, low	1 mm, low	1 mm, low
Deflagration test, rating	0.146 mm/s, no	16.7 mm/s, yes rapidly	0.105 mm/s, no
TPT, rating	1668 ms, yes slowly	467 ms, yes slowly	3557 ms, yes slowly

* Phlegmatizer E is Isopar V.

Phlegmatizer F is Isopar E.

5

The formulation of TBPA with Isopar V shows unacceptable PVT and deflagration test ratings. The composition according to the invention has improved PVT and TPT ratings compared to the formulation of TBPA with just Isopar E.

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Example 6 and Comparative Example G

	Example 6	Example G
MEKP content, (act. O)	8.92	8.92
Phlegmatizer, weight ratio *	H:G = 0.56:1	G
PVT, rating	1 mm, low	4 mm, medium
Koenen test, rating	1 mm, low	2 mm, violent
Deflagration test, rating	0.318 mm/s, no	0.190 mm/s, no
TPT, rating	2140 ms, yes slowly	820 ms, yes slowly

* Phlegmatizer H is Xylene.

Phlegmatizer G is Dimethylphthalate.

5

These examples demonstrate that commercial MEKP formulations based on MEKP can be improved by adding a low boiling phlegmatizer like xylene. Especially the negative effects of heating the composition in a confined space are dramatically reduced.

10

Examples 7 and 8

An accelerated blistering test was carried out at 50°C using the ASTM D714-56 method. Use was made of a turtle box which is a box with portholes closed off by means of a gel coated laminate, with the gel coat side facing the water in the box. The water in the box is stirred and controlled at the testing temperature. The gel coated laminate was produced by first casting a 400 µm (when dried) gel coat based on a commercial iso/npg unsaturated polyester resin system as supplied by De IJssel, and then a 2 mm lamination resin consisting of 70% ortho resin and 30% glass fibre. Both the gel coat system and the lamination resin were cured using 2% by weight of MEKP, based on the system and the resin, respectively. In Example 7, both the gel coat system and the lamination resin comprised 1% xylene. In Example 8, Example 7 was repeated except that the xylene was replaced by diethylene glycol. The amount of blistering is reported below.

Duration of test	Example 7	Example 8
4 weeks	no blistering	blistering started ASTM rating = 8, medium
12 weeks	no blistering	blistering progressed ASTM rating = 6, medium

Clearly, Example 7, representing a curing system in which one of the phlegmatizers of the peroxide composition is apolar, showed an improved resistance to blistering.

Example 9 and Comparative Example H

In Example 9 a composition was made consisting of methylethyl ketone peroxide and two phlegmatizers, viz. DMP and xylene (mixture of isomers).

- 5 The two phlegmatizers were used in a ratio of 56 % by weight and 44 % by weight, respectively, based on the total weight of the two phlegmatizers. In Comparative Example H, only one conventional phlegmatizer was used, viz. DMP. The products were evaluated for their viscosity using a thermostatted cone-plate type viscometer with a cone diameter of 28 mm
- 10 and a cone angle of 3° ex Tokyo Keiki Co. Ltd. Japan (type E) as well as their mixing behaviour with an unsaturated polyester resin at a temperature of 5°C (visual). The following results were obtained.

	Example 9	Comparative Example H
Act. O content (%)	9.45	10.25
Viscosity at 5°C (mPa.s)	8.3	45.7
Viscosity at 25°C (mPa.s)	4.1	17.0
Mixing behaviour	excellent	poor

- 15 The composition according to the invention clearly shows great advantages when used in processes where low viscosity and fast mixing with an unsaturated resin are required, such as in spray-on applications.

CLAIMS

1. A peroxide composition which is liquid at room temperature, having a rating of "low" or "medium" in the pressure vessel and Koenen test and showing no or slow deflagration, characterized in that it comprises at least two phlegmatizers that have boiling points more than 20°C apart, excluding combinations of ethylbenzene soluble di-tert-butylperoxy ketals with ethylbenzene and a higher boiling diluent.
2. A composition according to claim 1, characterized in that it comprises at least one peroxide selected from cyclic ketone peroxides, peroxyesters, diacylperoxides, peroxydicarbonates, peroxycarbonates, peroxyketals, dialkylperoxides, hydroperoxides, and combinations thereof.
3. A composition according to claim 1, characterized in that at least one of the peroxides is a non-cyclic ketone peroxide and at least one phlegmatizer is apolar.
4. A composition according to any one of claims 1-3 wherein at least one phlegmatizer is a hydrocarbon.
5. A composition according to any one of preceding claims 1-4, wherein the boiling point of the low boiling phlegmatizer is below 200°C.
6. A composition of any one of the preceding claims, wherein the peroxide is a ketone peroxide.

7. Use of a peroxide composition which is liquid at room temperature, having a rating of "low" or "medium" in the pressure vessel and Koenen test and showing no or slow deflagration, which comprises at least two phlegmatizers that have boiling points more than 20°C apart, for the curing of unsaturated polyester resins, and in processes involving the cross-linking, degradation or other modification of (co)polymers.
5
8. Use according to claim 7 wherein at least one phlegmatizer, preferably the low-boiling one, is apolar, for the curing of unsaturated polyester resins.
10
9. Use according to claim 7 or 8 wherein the peroxide is a non-cyclic ketone peroxide and involving the spray-on of unsaturated polyester resins.
15
10. Use of a peroxide composition according to any one of claims 1-6 in radical (co)polymerization processes.

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.
PCT/EP 98/00391

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C409/00 C07C409/22 C07D323/00 C08F4/38 C08K5/14
C08K5/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 072 728 A (WALLACE & TIERNAN INC.) 21 June 1967 cited in the application see the whole document	1
A	US 3 649 546 A (C.M. MCCLOSKEY ET AL.) 14 March 1972 cited in the application see the whole document	1
A	GB 1 470 012 A (CHINOOK CHEMICALS CORPORATION LIMITED) 14 April 1977 cited in the application see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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